Assessing the legacy of red mud pollution in a shallow freshwater lake: long-term chemical recovery in the water column

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Abstract

Little is known about chemical and ecological recovery following red mud leachate pollution in fresh waters. This is confounded by a lack of knowledge on the chemical composition of red mud leachate and the changes in composition that occur as a result of interactions with sediments and freshwater organisms during transport through aquatic ecosystems. We used over 30 years of data from a shallow lake (Kinghorn Loch, Fife, Scotland) with a well-documented history of several decades of red mud leachate pollution to characterise the chemical loads (during a pollution period of 1981-1983), resultant impacts on surface water chemistry (comparison between 1983 and 2009) and recovery trajectories following leachate diversion (1983-2010) of constituents that pose a risk to the environment. Between 1981 and 1983, the input of leachate resulted in loads of total aluminium (Al), total arsenic (As), total vanadium (V) and phosphate (PO_4-P) to the lake of 107, 2.3, 3.3 and 2.3 g m^{-2} (lake surface area) yr^{-1}, respectively. During the same period, the lake acted as a sink of Al, As, V and PO_4-P retaining 63.6, 0.6, 0.8 and 1.6 g m^{-2} yr^{-1}, respectively. We used General Additive Modelling to assess the response trajectories and recovery end points of these constituents. Our results demonstrate the complexity of sediment-pollutant interactions during pollutant transport through the aquatic environment and provide insight into likely recovery trajectories in other aquatic ecosystems following red mud contamination. The PO_4-P, total As and total V surface water concentration recovery times, defined statistically as the point on the time series beyond which no further significant decrease in concentrations were observed, ranged from 18 to 26 years. Total Al concentrations continued to decrease significantly following the end of the monitoring period in 2010. In Kinghorn Loch, the legacy of red mud pollution continues to represent an environmental risk, demonstrating the importance of long-term monitoring and management strategies following similar pollution events.

Key words: aluminium, arsenic, lake, phosphorus, recovery, vanadium

Introduction

The International Aluminium Institute, representing over 60% of global aluminium production industries report estimates of the global stock of red mud waste at 3,000 million tonnes (in 2010; Power et al., 2009, World Aluminium, 2015) with global production of about 120 million tonnes yr^{-1}. The effects of red mud pollution on aquatic ecosystems was demonstrated following a dam failure of a waste containment reservoir in October 2010 in Ajka, West Hungary. This resulted in the release of c.1 million m^3 red mud waste (Burke et al., 2012) which impacted a catchment area of 3078 km^2 (Klebercz et al., 2012). The highly alkaline pollution (pH 13.5) reached the Torna Creek and River Marcal, passed through the River Rába and entered the Danube, Europe's second longest river (Schöll and Szövényi 2011). Calcium sulphate was applied over large areas to reduce the effects of elevated pH in contaminated rivers and streams in following the incident in Hungary (Enserink 2010). Research soon after the spill focused on short-term chemical and ecological impacts in aquatic ecosystems and on the potential human health effects associated with airborne red mud particles. This showed a recovery in pH in the river systems almost 2 months after the pollution event, which decreased with distance from the source of pollution from c. pH 13 (at the site closest to the pollution source area) to c. pH 8 downstream. The presence of elevated concentrations of arsenic (As), molybdenum (Mo) and vanadium (V) in water and As, V, chromium (Cr), cobalt (Co) and nickel (Ni) in river sediment was limited to the Torna Creek and part of the upper Marcal River. The results indicated that in aquatic ecosystems with low residence times and well oxygenated surface sediments, red mud constituents including oxyanion forming elements (e.g. As, V, Cr) were contained within solid phase complexes and represented limited ecological threat. However, in depositional zones, where reducing redox conditions may be common, the liberation of such contaminants may be expected (Mayes et al., 2011).

74 To date, no study has been published documenting the longer term (i.e. years to decades)
75 recovery of any freshwater ecosystem, i.e. lotic or lentic, following red mud pollution. This
76 information is critical for the development of effective monitoring and management strategies
77 by the industry (World Aluminium, 2015). We propose that the current estimates of days to
78 months for chemical recovery (of As, V, aluminium (Al) and P) for all freshwater ecosystems
79 based on Mayes et al. (2016) are insufficient to cover all ecosystem types. Specifically, we
80 hypothesise that chemical recovery following red mud pollution in lakes (i.e. high residence
81 time depositional freshwater environments) will exhibit a long recovery time (i.e. similar to
82 years and decades commonly observed for P in lakes; Sharpley et al., 2013) in comparison to
83 the rapid recovery times (i.e. days to months) reported for fluvial systems following the Ajka
84 incident (Mayes et al., 2016). Our understanding of P recovery in lakes following
85 management for eutrophication indicates that recovery times can reach many decades as a
86 result of internal biogeochemical cycling, especially in ecosystems with high retention times
87 (i.e. lakes, wetlands and groundwater; Spears et al. 2012; Sharpley et al. 2013).

88 We tested this hypothesis using long-term monitoring data documenting chemical recovery in
89 Kinghorn Loch, UK, following red mud pollution control in 1983 (Olszewska et al., 2016).
90 The specific objectives of the study were to: (1) quantify the composition of red mud leachate
91 entering Kinghorn Loch during the peak pollution period in comparison to an unpolluted
92 surface water inlet (i.e. 1981 to 1983); (2) quantify the loads of Al, As, V and phosphate
93 (PO_4-P), and their retention by the lake; and (3) quantify recovery trajectories of red mud
94 pollutants following diversion of the leachate between 1983 and 2010. This information was
95 used in conjunction with environmental quality standards to assess the long-term
96 environmental risk associated with these pollutants and to revise estimates of recovery time
97 in freshwater ecosystems in general.

98

99 **Methods**

100 **Study site description**

101 Kinghorn Loch is a small lake of area 11.3 ha, mean depth 4.5 m and maximum depth 12.8
102 m, situated in Fife, Scotland (56°10′N; 3°11′W). For several decades the lake received
103 leachate from the nearby Whinnyhall landfill site where red mud waste from the Burntisland
104 plant of British Aluminium (BA) Ltd. was stored from 1944 (Fig. 1). This plant was in
105 operation from 1917 and by 1980 its production had risen to 120,000 t of alumina and
106 140,000 t of red mud waste per year, primarily through processing of bauxite from Awaso,
107 Ghana (Edwards, 1985). The landfill was drained through a series of ditches and culverts
108 which fed a retention pond of 60 m^3 capacity and 6 hours hydraulic retention time. The pond
109 was retained by a concrete dam with a V-notch flow-measuring weir delivering leachate
110 directly to Kinghorn Loch. Reports of failure of this retention pond to reduce loads of
111 suspended solids were common due to poor maintenance where the sluice plate was removed,
112 spilling solids and aqueous waste directly to the loch in pulses. This drainage system
113 delivered highly alkaline leachate from the landfill site to Kinghorn Loch, mixed with rain
114 and spring waters, from 1947 to 25 May 1983, when the discharge was diverted away from
115 the lake in a collaborative effort to improve water quality by BA Ltd. and the Forth River
116 Purification Board (FRPB). A second inflow to the loch, the North inlet was not
117 contaminated with leachate and represents background conditions for the catchment.

118 **Pollutant retention in Kinghorn Loch**

119 The frequency and nature of the sampling and analyses of the leachate, inlets and the outlet of
120 Kinghorn Loch are summarised in Table 1. It was assumed that the results from the Kinghorn
121 Loch outlet represented surface water conditions in the lake. The collection of water samples
122 and discharge measurements for the determination of pollutant loads was conducted between

April 1981 and September 1984 at weekly to fortnightly frequency. Discharge at the North and leachate inlets and downstream of the lake outlet were assessed by stage boards calibrated to discharge as described by Edwards (1985). Water samples were taken at mid-depth in running water in 1 and 10 L polythene or polypropylene bottles for metal and metalloid analysis and 1 L glass bottles for analysis of other determinands. The polythene and glass bottles were cleaned in 50% v/v nitric acid solution and 50% v/v chromic acid solutions, respectively, and rinsed with deionised water prior to sample collection.

Physico-chemical parameter measurements and sample filtration were conducted in the laboratory after sample collection. pH values were determined using a Radiometer PHM 63 meter. Alkalinity was measured by titrating 100 mL samples against a standardised 0.05 M sulphuric acid solution to pH 4.5, with leachate samples being diluted 1/10 with deionised water prior to the titration.

Water samples for the determination of dissolved calcium (Ca), magnesium (Mg), fluoride (F) and silica (SiO_2) concentrations were filtered through Whatman GF/C filters. Nitrate (NO_3-N), ammonium (NH_4-N), chloride (Cl), SiO_2, orthophosphate (PO_4-P), boron (B) and sulphate (SO_4-S) were determined using air segmented continuous flow analysis with photometric detection performed on a Technicon AutoAnalyzer II system based on the assay reviewed by the Standing Committee of Analysts (HMSO, 1980a). Detection limits for NO_3-N, NH_4-N, Cl, SiO_2, B and SO_4-S were 0.01, 0.04, 1.0, 0.1, 0.04, 2 mg L^{-1}, respectively. Detection limit for PO_4-P was 0.01 mg L^{-1} for the analysis of inlet and outlet samples, and 0.1 mg L^{-1} for the analysis of leachate. Fluoride concentrations were determined using an ion selective electrode with a separate standard calomel reference electrode, with a limit of detection of 0.01 mg L^{-1}.

Samples of leachate, inlets and outlet for dissolved metal and metalloid analyses were filtered through 0.1 μm polycarbonate filter membranes. 1 M spectrophotometric grade hydrochloric

148 acid was used to adjust pH to 2-4 in leachate samples for metal determination and 2 cm^3 L^{-1}
149 of hydrochloric acid was added to preserve all samples prior to analysis. The samples were
150 evaporated on a hotplate to approximately 80 cm^3 and made up to 100 cm^3 with deionised
151 water, concentrating the samples of leachate and North inlet by 10 and 100 times,
152 respectively. Dissolved and total metal and metalloid concentrations, apart from cadmium
153 (Cd) and lead (Pb), were determined using flame atomic absorption spectrophotometry
154 (Instrumentation Laboratories IL357 equipped with an IL254 autosampler) and based on the
155 method described in HMSO (1980b). Limits of detection for Al, Ca, Cr, copper (Cu), iron
156 (Fe), Mg, manganese (Mn), nickel (Ni), potassium (K), sodium (Na), V, As and zinc (Zn)
157 were 0.5, 0.005, 0.03, 0.01, 0.01, <0.002, 0.005, 0.02, 0.004, 1.0, 0.3, 0.005, 0.005 mg L^{-1},
158 respectively. Cd and Pb were measured by graphite furnace atomic absorption
159 spectrophotometry, with detection limits of 0.005 mg L^{-1} for Cd and 0.5 mg L^{-1} for Pb. Total
160 suspended solids (TSS) were determined by the removal of suspended matter from samples
161 using vacuum filtration, followed by drying at 105°C and reweighing. The limit of detection
162 for TSS was 2.5 mg L^{-1}.

163 The load of red mud associated contaminants to Kinghorn Loch was estimated using mean
164 discharge and determinand concentration data for each inlet and outlet in the 1981-1984
165 monitoring period outlined above. Annual loads were calculated for Al, total As, total V, and
166 PO_4-P prior to leachate diversion and used to estimate retention expressed relative to lake
167 surface area.

168 **Analysis of surface water and outlet determinands for analysis of long-term responses**

169 Surface water pH in Kinghorn Loch was measured by FRPB and BA Chemicals Ltd. between
170 1954 and 1981 typically up to 4 times per year. The methodology for pH used by BA
171 Chemicals Ltd. during this period is unreported, although we believe that water samples were
172 collected from the outlet prior to pH determination in a laboratory. The Scottish Environment

Protection Agency (SEPA) and FRPB (its predecessor) measured pH weekly between 1981 and 1984, and a suite of determinands monthly thereafter on water samples collected from the outlet, using standard methods (Table 1 and 2). Since no obvious discrepancy was apparent between the pH values measured by FRPB and BA Chemicals Ltd. data prior to 1981, we assume the methods were comparable.

Statistical analysis

A direct comparison was made between a wide suite of measured determinands to in 2009 (post-diversion conditions) versus 1983 (i.e. pre-diversion conditions). Low frequency of sampling in 2010 was the reason for using data from 2009 to represent post-diversion water quality. Data exploration showed violation of normality assumption. Therefore, a non-parametric Mann-Whitney-Wilcoxon test, which allows for normality violation, was used to assess the significance ($P < 0.05$) of the difference between the two years. The frequency of sampling and analysis by SEPA differed between the two years and was between 5 to 53 (depending on the determinand) in 1983 and 12 in 2009. Due to lack of measurements of Ca, Mg and Fe in 1983, data from 1981 were used for comparison for these determinands.

We used General Additive Models, assuming normal errors (GAMs, Hastie & Tibshirani, 1990; Wood, 2006), to determine the timing of recovery following diversion for determinands for which long-term data were available over a suitable time series. The endpoint of recovery was determined in two ways: (1) the year in which no further significant decrease in concentration was detected, as assessed using GAMs, and (2) the year in which the determinand concentration dropped below relevant ecological quality standards (where available) for the last time in the dataset.

For the GAM analysis, the aim was to identify relationships between the concentrations with year after the diversion of the red mud leachate, with season included as a fixed effect in the

197 analysis, the following modelling strategy was employed. A Gamma error structure (log link
198 function) was used in all models and an autocorrelation structure of AC1 (auto-regressive
199 model of order 1) on year relative to the diversion of the leachate from the inlet was applied.
200 The relationship between the response (pH and pollutant concentrations) and the explanatory
201 variable (year relative to the diversion of the pollution) was allowed to be a smooth function
202 instead of restricting the relationships to be linear. Due to the use of different smoothers for
203 different seasons for V and the significance of the fixed effect of season in the pH analysis,
204 separate models were fitted for different seasons for these two determinands. Data used in the
205 models were for the period 1981 – 2009 (the last two years of the pollution input and the
206 recovery period that followed). Based on the recommendations of Zuur et al. (2009) the
207 response variables were not transformed prior to analysis. The changes in the red mud
208 constituent concentrations were compared against relevant ecological quality standards. As
209 there is no standard for PO_4-P or total phosphorus (TP) for Kinghorn Loch, the Trophic State
210 Index for TP (Carlson et al., 1996) was used to provide ecological context for the lake water
211 TP concentrations. Due to the lack of ecological quality standards for total As and Al, the
212 results were compared against the standards for dissolved As and reactive Al, respectively.
213 As such, our comparisons of total element concentrations against EQSs should be considered
214 the worst case scenario. In reality the risk associated with dissolved components of the total
215 element concentration will be lower. The models were fitted using the GAM function in the
216 mgcv package (1.7-6) (Wood, 2011) and statistical analyses were conducted using R version
217 2.15.1. (R Core Team, 2012) available at http://www.r-project.org.

Results

Red mud loading to Kinghorn Loch

Prior to the diversion of the red mud leachate from Kinghorn Loch pH and alkalinity at the leachate inlet were 12.1 and 4125 mg L^{-1} (i.e. mean values 1981-1983), respectively, compared to 8.1 and 133 mg L^{-1}, respectively, for the north inlet (Table 3). The leachate inlet was characterised by high concentrations of Al, V, As, Zn, Cu, Pb, Cr, Cd, Fe, K, Cl, F, SO_4-S, Na, PO_4-P and TSS compared to the north inlet. North inlet water contained higher concentrations of Ca and Mg compared to the leachate inlet. The load from the leachate inlet of total Al, As, V and PO_4-P to the lake during the period January 1981 to May 1983 was 107, 2.3, 3.3 and 2.3 g m^{-2} yr^{-1}, respectively. The annual retention of Al, As, V and PO_4-P was 63.6, 0.6, 0.8 and 1.6 g m^{-2} yr^{-1}, respectively.

Lake water chemical responses following red mud leachate diversion

pH in Kinghorn Loch outlet water increased until the diversion of the leachate in 1983, reaching a value of 10.5 (Fig. 2). Following diversion, pH decreased in the first few years before clear seasonal patterns emerged (higher pH values in summers, lower in winters), with pH fluctuating between 7.5 and 9.5. All measured determinands in the lake outlet water were significantly lower in 2009 than in 1983, with the exception of total Ca and Mg which had significantly higher concentrations in 2009 than in 1983 (Table 4, Figs. 3-4). Concentrations of total Fe, As and V were < 1 mg L^{-1} in 1983 and, together with total Al, decreased to < 0.1 mg L^{-1} in 2009. Concentrations of PO_4-P decreased from 0.076 to 0.012 mg L^{-1} between 1983 and 2009.

Recovery trajectories for pH, phosphorus, aluminium, arsenic and vanadium

240 The time series of concentrations of total Al, total As, total V and PO_4-P before and after the
241 diversion are shown (Fig. 4). For all these determinands, concentrations decreased following
242 the diversion in May 1983 until 1985 after which the rate of decrease slowed, with occasional
243 high concentrations occurring. GAMs showed that the recovery times were determinand-
244 specific and that the effects of season were significant for total V and pH. Our analysis
245 indicated that no further significant decrease in pH values occurred 5 years following
246 leachate diversion (Table 5). Declines in PO_4-P concentrations ceased in 2007 and, although
247 not directly comparable, PO_4-P concentrations were below the suggested Trophic State Index
248 value for TP of 0.024 mg L^{-1} (Carlson et al., 1996) by 1986 (0.020 mg L^{-1}). For total Al, the
249 significant decrease in concentrations was maintained until the end of the observation period
250 in 2009 when the Al concentration still exceeded the ecological quality standard of 0.015 mg
251 L^{-1} (SEPA Supporting Guidance, 2013). Total As concentrations declined following leachate
252 diversion for a period of 22 years, with concentrations falling below the water quality
253 guideline of 0.050 mg L^{-1} (UK Standards for Protection of Aquatic Life; EEC, 1976) in 2006.
254 Depending on the season, it took from 18 to 26 years for the total V concentrations to stop
255 significantly decreasing, with the shortest recovery period observed for autumn and the
256 longest for spring and winter. Concentrations of total V measured in autumn decreased to
257 below the water quality guideline of 0.020 mg L^{-1} for total V (UK Standards for Protection of
258 Aquatic Life; EEC, 1976) in 2001, whilst spring concentrations only fell below the guideline
259 value in 2008.

260

Discussion

Impacts of red mud leachate on lake chemistry

The composition of the red mud leachate, which entered Kinghorn Loch between 1947 and 1983, posed four potential pressures on the aquatic environment: high pH, metal and metalloid pollution, eutrophication and high salinity. The high loadings of contaminants entering the lake (e.g. 107, 2.3, 3.3 and 2.3 g m^{-2} yr^{-1} of total Al, As, V and PO_4-P, respectively) led to high concentrations of a range of metals (e.g. total Al - 7.30 mg L^{-1}, V – 0.49 mg L^{-1}), metalloids (e.g. As – 0.32 mg L^{-1}), PO_4-P (0.13 mg L^{-1}) and chloride (38.0 mg L^{-1}) in the loch water. The concentrations of some pollutants in the water column in 1983 greatly exceeded ecological quality standards for fresh waters. Specifically, the concentrations of PO_4-P and total As were approximately 3 and 5 times higher than the relevant environmental guidelines, whilst total V and total Al concentrations were 22 and 355 times higher, respectively, than the recommended ecological quality values. The pressures in Kinghorn Loch, with the exception of eutrophication, were also observed in the river system downstream of the Ajka red mud spill in Hungary in 2010 (Mayes et al., 2011; Ruyters et al., 2011; Shöll and Szövényi, 2011).

Recovery following red mud pollution

The results of the GAM analyses indicated that chemical recovery in Kinghorn Loch took decades to complete and is in agreement with our hypothesis based on P recovery following eutrophication management. The time scale of the recovery differed among the determinands. The shortest recovery period (5 years) was observed for pH. In contrast, analysis of the river system affected by the Ajka red mud spill indicated rapid recovery in pH only 2 months after the pollution accident at sites further downstream from the pollution source (Mayes at al., 2011). The fast improvement in pH in this case was, however, a result of both acid dosing

285 and dilution of the contaminated water in the river system (Mayes et al., 2011), whereas no
286 remedial actions were taken in Kinghorn Loch. In addition, elevated pH in Kinghorn Loch
287 during the first few years following the cessation of pollution may have been influenced by
288 the enhanced phytosynthetic activity in the lake (Scheffer, 2004).

289 As a result of eutrophication caused by high P loading, intense phytoplankton blooms
290 occurred in Kinghorn Loch from the mid-1970s until 1985, when a collapse in the
291 phytoplankton activity was recorded (Edwards, 1985). These results indicate that the
292 recovery times reported following the Ajka spill are not representative of all freshwater
293 ecosystems. In addition, we report here significant differences in the long term recovery
294 times for Al, As, V, and PO_4-P ranging from 18 to 26 years, with significant seasonal effects
295 being reported for V. Sporadic peaks in contaminant concentrations can be observed even in
296 recent years in Kinghorn Loch indicating persistent environmental risk, especially associated
297 with PO_4-P, total V, As and Al. Olszewska et al. (2017), using laboratory controlled sediment
298 core incubations confirmed the release of P, As and V from bed sediments in recent years,
299 being controlled predominantly by redox conditions, competitive ion concentrations and pH.

300 Delayed recovery following pollution control has been well documented in the case of P in
301 lakes (Jeppesen et al., 2007; Søndergaard et al., 2003, Spears et al., 2012), and also for As
302 (Toevs et al., 2008; Whitmore et al., 2008) and V in fresh waters (Minelli et al., 2000).
303 Competition between P, As and V for adsorption to iron oxyhydroxides may lead to
304 preferential immobilisation of these pollutants in bed sediments (Wällstedt et al., 2010). High
305 pH can also have negative effects on immobilisation of some elements, e.g. P (Søndergaard et
306 al., 1999) and V (Naeem et al., 2007) and might therefore account for longer recovery times.
307 The likely impact of the elevated pH in Kinghorn Loch in the years immediately following
308 the diversion of the leachate, as well as the potential competition for sorption sites between
309 some red mud constituents, indicate that these interactions may be a dominant factor

310 regulating chemical recovery. However, uptake into biota may also be a major pathway of
311 internal cycling of red mud pollutants; significant accumulation of As species was reported in
312 tissues of macrophytes in Kinghorn Loch, as recently as 2013 (Olszewska et al., 2016).

313 Concentrations of most determinands were significantly lower in 2009 than in 1983, with the
314 exception of Mg and Ca, and PO_4-P, As and V concentrations were all below the relevant
315 ecological quality standards in 2009, although total Al was not. Mg and Ca concentrations
316 were significantly higher in 2009 than in 1983 (15.9 and 24.5 mg L^{-1} in 2009, respectively,
317 compared to 8.80 and 7.12 mg L^{-1} in 1983), although the major input of these two elements
318 was the unpolluted north inlet, characterized by high natural levels of water hardness. The
319 significantly lower concentrations of Mg and Ca in lake outlet water in 1983 were likely to be
320 a result of removal of any free Ca^{2+} and Mg^{2+} by reaction with the high carbonate alkalinity
321 coming from the leachate to form solid carbonates in the elevated pH conditions (Renforth et
322 al., 2009).

323 **Implications for management**

324 Mayes et al. (2011) reported rapid contaminant dilution, with the exception of depositional
325 hotspots, in the river system affected by the Ajka accident, indicating species-specific
326 transport rates through the system (Mayes et al., 2011). Although chemical recovery was
327 reported to be rapid, good ecological condition in the Torna Stream polluted in the Hungarian
328 accident is not expected to be achieved until 2021, some 11 years after the pollution event
329 (Kovács et al., 2012). Our results indicate that chemical recovery time may be significantly
330 longer in depositional zones with long hydraulic retention times. Ecological recovery times
331 may be longer still. The analysis of As content in five macrophyte taxa in Kinghorn Loch
332 conducted in 2013 showed that macrophytes contained relatively high concentrations of toxic
333 inorganic As, suggesting toxicological risk to higher trophic levels (Olszewska et al., 2016).

There appears to be a lack of evidence on available measures with which to mitigate the environmental impacts of red mud pollution in lakes. In Hungary, calcium sulphate was applied (Enserink 2010) to reduce the pH effects. In Kinghorn Loch, metal concentrations remained elevated above environmental quality standards even after pH had recovered and so pH control only may be insufficient to control the effects of complex potentially harmful elements in fresh waters as confirmed also by Mayes et al. (2016).

Removal of contaminated sediments has been practiced as a measure for mitigating environmental impacts of metals and nutrients in lakes with mixed effectiveness (Peterson, 1982; Phillips et al., 2015). Emerging geo-engineering techniques (Spears et al. 2013; Lürling et al., 2016) developed for the simultaneous control of multiple elements may also represent effective management tools in this respect for oxyanion forming elements (e.g. As, V, P), although the development of this approach is in its early stages. Aeration of bottom waters may also be effective in the control of redox sensitive elements, including As and P (Beutel and Horne, 1999). Advances have been made recently in the development of materials with which to deliver oxygen to lake bed sediments. Nykänen et al. (2012) have demonstrated at the field scale the application of calcium peroxide to manipulate redox conditions at the bed sediment surface which can lead to the reduction of P release to the water column (Lu et al., 2017). However, oxidising conditions might result in undesirable response in V, leading to a release of this metal from bed sediment, as shown by Olszewska et al. (2017). We call for a more comprehensive assessment of such measures to support emergency response strategies and longer-term mitigation options.

Conclusions

- A significant decrease of pH and concentrations of all red mud constituents occurred in Kinghorn Loch water after leachate was diverted from the loch inflow waters.
- The chemical recovery period of PO_4-P and total V, As and Al ranged from 22 to 26 years, depending on the determinand, and was 5 years for pH. Total Al concentrations had not reached the end-point of recovery after 26 years.
- Evidence of persistent cycling of PO_4-P total V, As and Al between bed sediments and the water column appears to be the major process regulating recovery.
- The higher retention time of standing waters can result in longer chemical recovery times following red mud pollution in lakes compared to rivers and streams.

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List of Figures

Fig. 1. Locations of the former production plant and landfill site, and current location of the treatment plant in relation to Kinghorn Loch (image courtesy of Google Earth, taken in 2010).

Fig. 2. Long-term trends in water pH in Kinghorn Loch. The shaded area represents the period of recovery following diversion of leachate from the lake inlet.

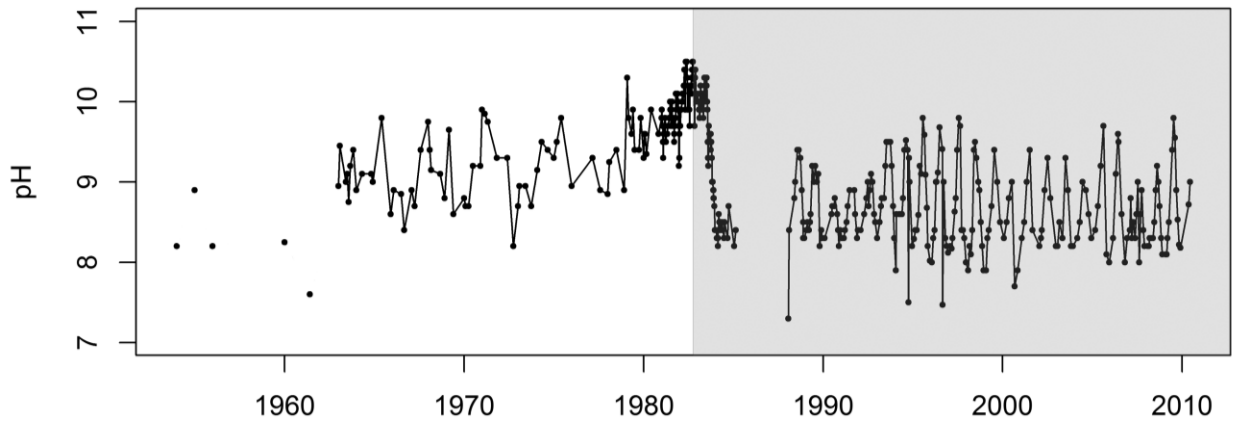

Fig. 3. Concentrations of pollutants in Kinghorn Loch outlet in 1983 (prior to diversion of the leachate) and in 2009 (after 26 years of recovery). Due to no measurements of Ca, Mg and Fe in 1983, data from year 1981 were used for these three determinands. Data are summarised as boxplots showing the median and 25th and 75th quartiles, with whiskers representing the values outside the middle 50% and outliers shown as dots.

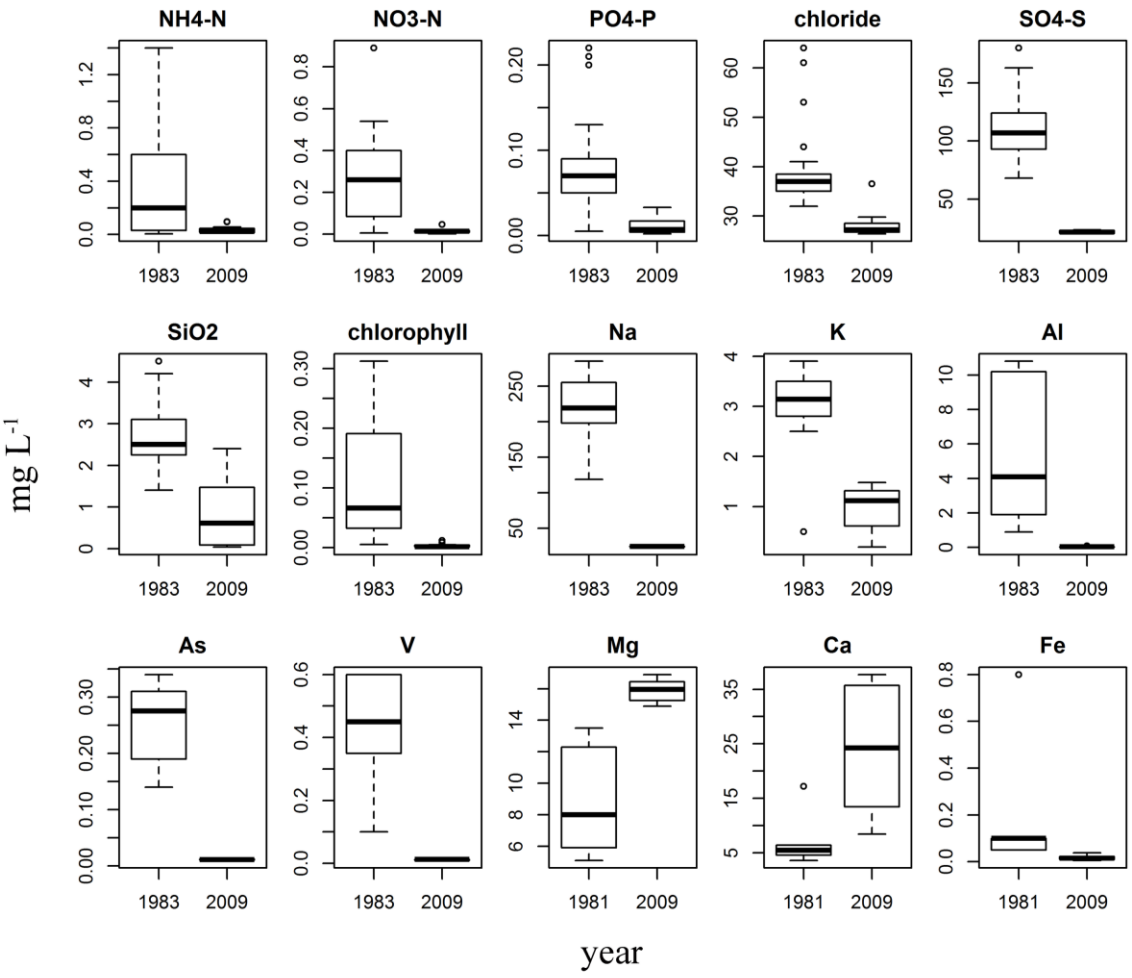

Fig. 4. pH, conductivity, alkalinity and TSS in Kinghorn Loch outlet in 1983 (prior to diversion of the leachate) and in 2009 (after 26 years of recovery); recovery). Data are summarised as boxplots showing the median and 25th and 75th quartiles, with whiskers representing the values outside the middle 50% and outliers shown as dots.

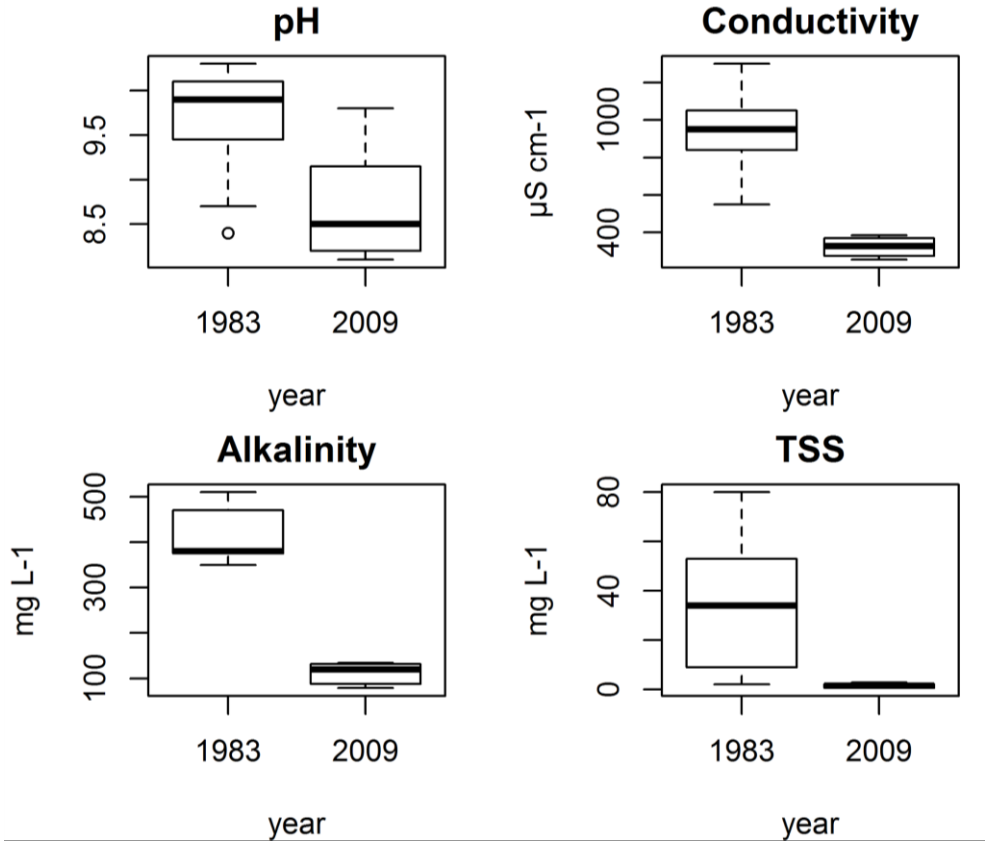

Fig. 5. Total arsenic (panel a), vanadium (panel b), aluminium (panel c) and orthophosphate (PO_4-P, panel d) concentrations in Kinghorn Loch outlet prior to (1981-1983) and following (1984-2010) the diversion of the leachate from the loch inlet in 1983. Vertical dashed lines indicate the cessation of red mud leachate input into the lake in 1983.

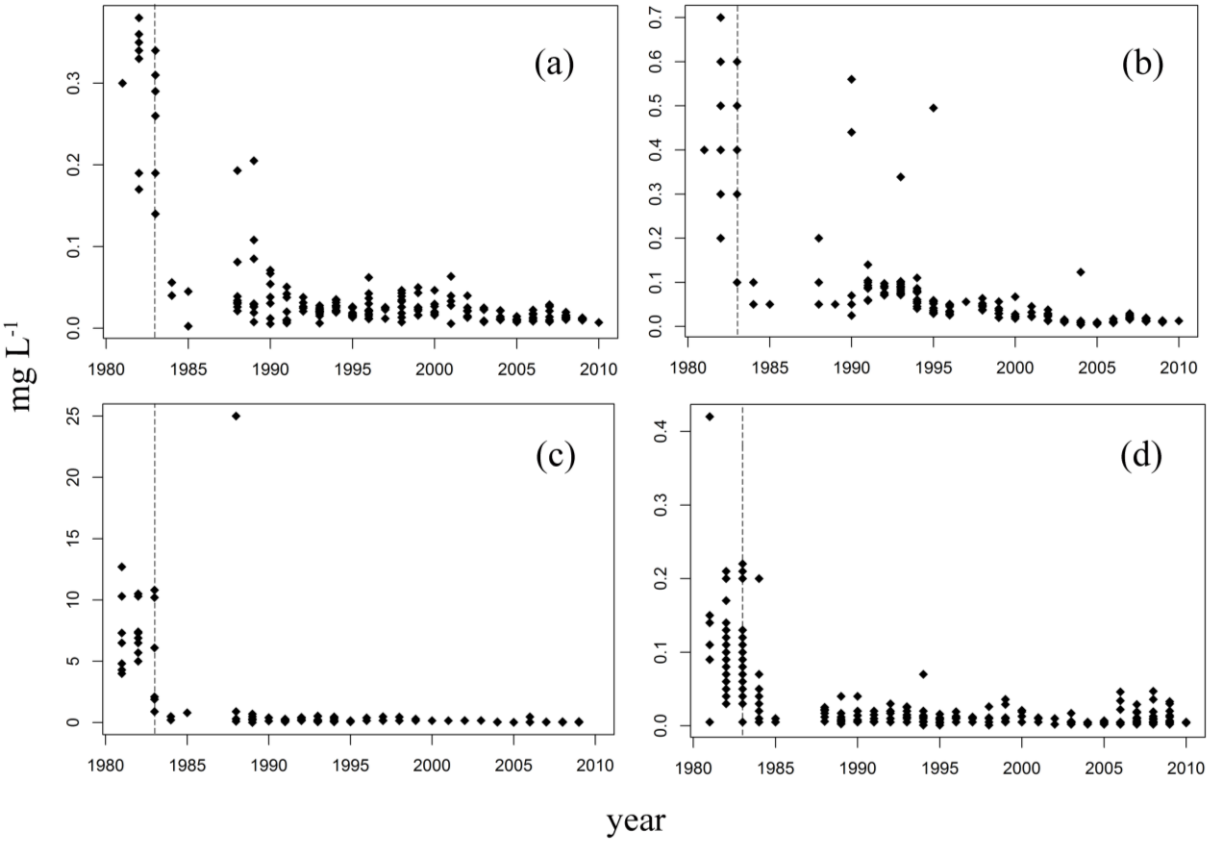

Table 1. Summary of leachate and Kinghorn Loch inlet and outlet sampling and analysis conducted to 2010.

Time period	Frequency	Location	Measurements and analyses	Samples collected by:
1976-1981	up to 4 times per year	incoming leachate	pH, chemical composition	Forth River Purification Board (FRPB) and BA chemical Ltd.
1954-1981	up to 4 times per year	lake outlet	pH	FRPB and BA Chemical Ltd.
Apr 1981-Sep1984	weekly - fortnightly	incoming leachate	temperature, pH, conductivity,, major ions, trace elements (total and dissolved), TSS, chlorophyll a, discharge	Edwards (1985) and FRPB
Apr 1981-Sep 1984	weekly - fortnightly	North inlet	temperature, pH, conductivity, BOD, major ions, trace elements (total and dissolved), TSS, chlorophyll a, discharge	Edwards (1985) and FRPB
Apr 1981-Sep 1984	weekly - fortnightly	lake outlet	DO, temperature, pH, conductivity, alkalinity, BOD, COD, , major ions, trace elements (total and dissolved), TSS, chlorophyll a, discharge	Edwards (1985) and FRPB
1981-2010	weekly – 6 times per year	lake outlet	DO, temperature, pH, conductivity, alkalinity, BOD, COD, major ions, trace elements (total and dissolved), TSS, chlorophyll a	Scottish Environment Protection Agency (SEPA) and FRPB (its predecessor)

Table 1. Procedures used by SEPA for the analyses of Kinghorn Loch outlet water during the period 1981 to 2010.

Determinand	**Procedure based on:**
pH, alkalinity as $CaCO_3$, electrical conductivity	HMSO. 1981. The Determination of Alkalinity and Acidity in Water, 1981 - Methods for the Examination of Waters and Associated Materials. London.
Total Suspended Solids	HMSO. 1984. Suspended, Settleable and Total Dissolved Solids in Waters and Effluents, 1980 - Methods for the Examination of Waters and Associated Materials. London.
chlorophyll a	HMSO. 1983. The Determination of Chlorophyll a in Aquatic Environments, 1980. Methods for the Examination of Waters and Associated Materials. London; 13.2 ISO 10260: 1992(E). Water quality - Measurement of biochemical parameters – Spectrometric determination of the chlorophyll-a concentration. 9pp. International Organization for Standardization, Genéve
NH_4	HMSO. 1982. Ammonia in Waters, 1981 - Methods for the Examination of Waters and Associated Materials. London.
NO_3-N	HMSO. 1982. London. Oxidised Nitrogen in Waters 1981 - Methods for the Examination of Waters and Associated Materials. London.
PO_4-P	HMSO. 1981. Based on Phosphorous in Waters, Effluents and Sewages, 1980 - Methods for the Examination of Waters and Associated Materials. London.
chloride	HMSO. 1982. Chloride in Waters, Sewage and Effluents 1981 - Methods for the Examination of Waters and Associated Materials. London.
SO_4-S	HMSO. 1989. Based on Sulphate in Waters, Effluents And Solids (2nd Edition) 1988 - Methods for the Examination of Waters and Associated Materials. London.
SiO_2	HMSO. 1981. Silicon in Waters and Effluents 1980 - Method For The Examination Of Waters And Associated Materials. London.
Metal and metalloids	HMSO. 1996. Inductively Coupled Plasma Spectrometry 1996, Methods for the Examination of Waters and Associated Materials. London.

Table 3. Mean values and loads for determinands measured (generally weekly to fortnightly) in Kinghorn Loch inlets and the outlet during the period 4 April 1981 to 24 May 1983. Bold values are from single spot samples. Filtered samples are shown in brackets with < denoting a value that is lower than the detection limit. Data from spot samples collected from Torna Creek (Hungary) on 1 December 2010 are shown for comparison (from Mayes et al., 2011).

Determinand	**Leachate inlet** (mg L^{-1})	**North inlet** (mg L^{-1})	**Loch outlet** (mg L^{-1})	**Leachate load** (g m^{-2} yr^{-1})	**Pollutant retention in the loch** (g m^{-2} yr^{-1})	**Torna site K1** (mg L^{-1})
pH	12.1	8.1	9.9			13.1
Alk	4125	133	427	3038		7160
TSS	87	6.2	31	66		
NH_4-N	(0.7)	(0.14)	(0.26)	(0.50)		
NO_3-N	(1.8)	(7.3)	(1.8)	(1.4)		
PO_4-P	(3.0)	(0.04)	(0.13)	(2.3)	1.6	
SO_4-S	154	23	44	114		727
Cl	68	26	38	52		83
SiO_2-Si	(7.1)	(4.6)	(1.2)	(5.1)	23.72	499 (0.67)
F	3.2	0.15	1.5	2.7		
Ca	7.2 (4.0)	51 (43)	11 (3.4)	4.8 (3.1)	232.7	1515 (1.3)
Mg	8.2 (0.10)	25 (22)	10 (4.3)	6.1 (0.72)	101.8	9.7 (0.001)
Na	(2007)	(21)	(252)	(1514)		(701)
K	(26)	(0.67)	(3.7)	(19)		115 (85)
Fe	0.51 (0.12)	0.19 (0.08)	0.13 (0.06)	0.30 (0.09)		10 (<0.01)
Al	138 (138)	0.38 (0.17)	7.3 (6.6)	107 (1.5)	63.6	1228 (659)
As	3.6	0.01	0.32	2.3	0.60	3.9 (3.61)
V	5.3	0.05	0.49	3.3	0.76	6.4 (5.7)
Zn	**0.01**					0.5 (0.05)
Cu	**0.03**					0.4 (0.31)
Pb	**0.03**					0.3 (0.04)
Mn	**0.06**					9.9 (<0.001)
Ni	**0.06**					0.3 (0.04)
Cr	**0.11**					0.4 (0.05)
Cd	**0.01**					0.1 (0.05)
B	0.82	0.06	0.13	0.59	0.14	1.0 (0.90)

Table 4. Results of Mann-Whitney-Wilcoxon tests to assess the significance of the difference between determinand values in lake outlet water in 1983 (prior to diversion of the leachate) and in 2009 (after 26 years of recovery). Due to no measurements of Ca, Mg and Fe in 1983, data from year 1981 ([a]) were used for these three determinands.

Response variable	1983 ([a]1981)			2009			Test of difference	P-value
	Mean value	S.D.	n_1	Mean value	S.D.	n_2		
pH	9.70	0.526	53	8.69	0.625	11	512	< 0.001
Alkalinity as $CaCO_3$ (mg L^{-1})	417	69.1	5	112	22.9	11	55	0.002
Conductivity (µS cm^{-1})	936	148	53	325	49.3	12	636	< 0.001
Total Suspended Solids (mg L^{-1})	32.8	23.2	53	1.44	0.921	12	632	< 0.001
Chlorophyll a (µg L^{-1})	108	94.2	37	3.15	3.53	12	437	< 0.001
(mg L^{-1})								
NH_4-N	0.359	0.405	50	0.036	0.030	12	464.5	0.003
NO_3-N	0.259	0.192	47	0.015	0.011	12	517	< 0.001
PO_4-P	0.076	0.045	47	0.012	0.011	11	507.5	< 0.001
SO_4-S	108	23.7	49	21.8	1.25	12	588	<0.001
Chloride	38.0	6.23	47	28.3	2.788	12	541	< 0.001
SiO_2	2.66	0.738	50	0.858	0.913	12	555.5	<0.001
Ca[a]	7.12	5.05	6	24.5	11.5	12	4	0.001
Mg[a]	8.80	3.60	6	15.9	0.686	12	0	<0.001
Na	221	36.4	49	24.5	0.522	12	588	< 0.001
K	3.12	0.539	49	0.961	0.439	12	579	< 0.001
Fe[a]	0.220	0.325	5	0.017	0.010	12	60	<0.05
Al	5.33	4.38	6	0.034	0.018	12	72	< 0.001
As	0.254	0.072	8	0.011	0.001	12	96	< 0.001
V	0.438	0.177	8	0.012	0.002	12	96	< 0.001

Table 5. Summary of generalised additive modelling (GAM) results for red mud contaminant recovery trajectories in Kinghorn Loch outlet water. Optimal models for total V and pH predicted different recovery times for different seasons due to the use of separate smoothers for each season in the total V model and the significance of the fixed effect of season in the pH model.

Response variable	r^2 adj	n	P-value	Deviance (%)	Recovery time (years)	End point value (mg L^{-1})	Season	Ecological quality guidelines (mg L^{-1})
PO_4-P	0.68	231	<0.001	60.8	24	0.004	-	0.024
Total Al	0.70	146	<0.001	87.5	26	0.020	-	0.015
Total As	0.79	192	<0.001	-	22	0.016	-	0.050
Total V	0.53	190	<0.001	83.2			-	0.020
					20	0.017	summer	
					18	0.018	autumn	
					26	0.010	winter	
					26	0.019	spring	
pH	0.58	237	<0.001	60.3				
					5	9.05	summer	
					5	8.57	autumn	
					5	8.28	winter	
					5	8.63	spring	